10

Holland, E.A., G.P. Robertson, J. Greenberg, P. Groffman, R. Boone, and J. Gosz. 1999. Soil CO_2, N_2O, and CH_4 exchange. Pages 185-201 *in* G.P. Robertson, C.S. Bledsoe, D.C. Coleman, and P. Sollins, eds. Standard Soil Methods for Long-Term Ecological Research. Oxford University Press, New York.

Soil CO_2, N_2O, and CH_4 Exchange

Elisabeth A. Holland
G. Philip Robertson
James Greenberg
Peter M. Groffman
Richard D. Boone
James R. Gosz

The composition of the earth's atmosphere is largely determined by the exchange of trace gases with the oceanic and terrestrial biosphere. Human-induced perturbations to the earth's system are changing the atmospheric composition at unprecedented rates. The gases of particular interest can be divided into two categories: those species that are radiatively active and thus influence the radiation balance of the earth (the so-called greenhouse gases: nitrous oxide [N_2O], carbon dioxide [CO_2], methane [CH_4], chlorofluorocarbons [CFCs], halogenated chlorofluorocarbons [HCFCs], and ozone [O_3]), and those species that are photochemically active and thus influence the troposphere's ability to cleanse itself (its "oxidizing capacity": hydroxyl radical OH, hydroperoxy radical HO_2, O_3, active nitrogen (NO_x–NO + NO_2), carbon monoxide [CO], CH_4, and volatile organic carbon compounds other than methane [VOCs]). The atmospheric lifetime of the radiatively active species is often longer than 10 years, extending to as long as 120 years for N_2O in the troposphere (the lower 10–16 km of the atmosphere), whereas the lifetime of the photochemically active species is 1–3 days (Tab. 10.1). Because of their very long lifetimes, N_2O, CFCs, HCFCs, and other halogenated compounds persist long enough to be transported to the stratosphere, where they play an important role in stratospheric ozone depletion. Some gases, notably O_3 and CH_4, are both photochemically and radiatively active. Both radiatively active and photochemically active gases are central to global change research; these gases are rapidly altering atmospheric composition and chemistry, in part as a result of changes in biospheric activity.

Trace gas exchange can also provide an important pathway for ecosystem inputs and losses of nitrogen and carbon. Methane emissions constitute 7% of annual aboveground net primary productivity for wetlands (Aselmann and Crutzen 1989).

Table 10.1. Summary of Some Greenhouse Gases Affected by Human Activity Including Concentration, Lifetimes, and Rates of Increase

	CO_2	CH_4	N_2O	CFC-12
Preindustrial concentration	280 ppm_v	700 ppb_v	275 ppb_v	zero
Concentration in 1992	335 ppm_v	1714 ppb_v	311 ppb_v	503 ppt_v†
Recent rate of increase				
1980s	0.4%/yr	0.8%/yr	0.25%/yr	4%/yr
1990–1992	0.1%/yr	0.27%/yr	0.16%/yr	—
Atmospheric lifetime (years)	(50–200)††	(12–17)†††	120	102

†ppt_v = part per trillion by volume.
††No single lifetime for CO_2 can be defined because of the different rates of uptake by different sink processes.
†††This has been defined as an adjustment time which takes into account the indirect effect of methane on its own lifetime.

Nitrogen gas losses (NH_3, NO_x, N_2O, and N_2) can be as much as 50% of fertilizer input into agricultural ecosystems and may be equally significant in unmanaged ecosystems. Models that do not incorporate these loss pathways can substantially overestimate net primary production (NPP) and long-term storage of both carbon and nitrogen (Schimel et al. 1997; W. Parton and W. Hunt, personal communications). NO_x and ammonia inputs to the atmosphere generate nitrogen deposition elsewhere. Nitrogen deposition is increasing exponentially, with a total of 80 Tg y^{-1} of N deposited on today's earth (Holland et al. 1997). Quantification of both inputs and loss pathways is central to describing the state of an ecosystem as well as possible trajectories for change.

In this chapter we focus on the measurement of the exchange, or the net flux, of radiatively active gases that are produced and consumed in soils of natural and agricultural ecosystems: CO_2, N_2O, and CH_4. The specific processes responsible for the production and consumption of these gases is treated in other chapters of this volume, including Chapters 11, 13, and 14. Without exception, the estimated global budget of each of these trace gases has changed substantially as we have incorporated the results of research performed between the late 1980s and the mid-1990s (IPCC 1995). The rates of atmospheric increase for the three gases have been dynamic (Tab. 10.1). One of the most variable terms in each budget has been the estimated fluxes from natural and agricultural ecosystems. Terrestrial biogenic sources are thought to constitute between 40% and 80% of the global sources of these gases (depending on the gas) and are known to be dynamic, but controls as well as patterns of fluxes are poorly known. Thus, periodic measurements using standard techniques at a variety of sites will provide much needed information.

Available Methods

A wide variety of techniques are available for the measurement of trace gases on spatial scales that range from a single point to measurements that can be integrated

over square kilometers. At the finest scale there are measurements of soil atmosphere concentrations using probes (stainless steel or Teflon tubes) placed at various depths in the soil. For flux measurements at spatial scales ranging from 0.1 to 1.0 m^2, enclosures (chambers) are placed on the surface of the soil, allowing gas to accumulate over time and enabling the calculation of accumulation. For flux measurements at larger spatial scales, fluxes can be estimated using micrometeorological measurements on towers. Such measurements characterize the vertical gradient and flux of a gas integrated over areas ranging from 0.5 to 100 ha (spatial scales for this method are dependent on the height of the measurements). Although they are not flux measurements, Fourier transform infrared (FTIR) spectrometer and differential absorption (LIDAR) measure gas concentrations and integrate over distances as long as several kilometers . Aircraft sampling integrates over a larger surface area; the footprint of integration depends on both the flight altitude and meteorological conditions (Matson and Harriss 1995; Desjardins et al. 1993).

When compared, different methods provide similar estimates of fluxes. Aircraft and tower flux measurements of carbon dioxide fluxes over the Konza LTER tallgrass prairie were highly correlated (Desjardins et al. 1993). Comparison of N_2O fluxes using different chamber techniques (closed versus open and chambers of different volumes), different micrometeorological techniques (eddy covariance, flux gradient and conditional sampling using two tunable diode lasers [TDL], an FTIR and a gas chromatograph), and chamber versus micrometeorological techniques show reasonable agreement provided the patchiness of the landscape is taken into account when examining micrometeorological measurements from different wind directions (Christensen et al. 1996; Hargreaves et al. 1996; Ambus et al. 1993).

The two most frequently used techniques for measuring surface-atmosphere gas exchange are micrometeorological and enclosure techniques. For experiments where the goal is to produce an estimate of trace gas exchange over large areas (greater than a few square meters), micrometeorological techniques are preferable because they incorporate much of the meter-to-meter variation (Lenschow 1995; Baldocchi 1991). Micrometeorological techniques have evolved considerably, and there are now methods for avoiding the stringent sampling requirements and sampling frequencies of eddy correlation measurements (Lenschow 1995; Businger and Oncley 1990). Multiyear deployments of eddy flux measurements at the Harvard Forest LTER have been highly successful in providing insights in regional carbon exchange and storage on both an intra-annual and an interannual basis (Goulden et al. 1996; Wofsy et al. 1993). Enclosure (chamber) techniques enable the study of factors driving meter-to-meter variation in fluxes, facilitate manipulative studies, and are often a critical complement to eddy flux measurements.

We recommend enclosure techniques because they are relatively inexpensive, simple to operate, require less data analysis and manipulation than micrometeorological methods, and use equipment that can easily be moved from one location to another, thus allowing sampling of many locations within a landscape. As is pointed out in many other chapters in this volume, the scientific question posed is the primary determinant of the choice of techniques and the optimal experimental design.

Enclosure Technique for Measuring CO_2, CH_4, and N_2O Fluxes

Enclosure designs are of two basic types, static and flow-through. Static designs typically contain a small port to permit sampling and a small vent to permit equilibration of internal and external atmospheric pressures. Flow-through designs may be steady-state (in which the enclosure is swept with air drawn from a source of known concentration resulting in a "steady" concentration gradient across the air-soil interface within the enclosure) or non–steady-state (in which the trace gas concentration gradient diminishes in response to continual concentration changes within the enclosure). Static chambers such as those recommended here are by nature non-steady-state enclosures. A review of the possibilities and the considerations needed for each type of enclosure is provided in Denmead (1979), Kanemasu et al. (1974), Jury et al. (1982), Hutchinson and Livingston (1993), and Livingston and Hutchinson (1995). The most commonly used technique for measurement of N_2O and CH_4 fluxes is to periodically sample a static vented chamber with subsequent gas chromatographic analysis of the gas sample (Fig. 10.1).

Materials

1. Permanent collars made of PVC, stainless steel, or aluminum. See below for design recommendations.
2. Soil knife to circumscribe collar location (optional depending on the type of site)
3. Enclosures with a vent, sampling port, and a mechanism for securing and sealing to permanent collars (see section on "Enclosure and Collar Design and Construction," below and Fig. 10.1)
4. Seven conditioned polypropylene or nylon syringes fitted with one-way stopcock valves to transport gas samples to laboratory (and storage vials if the gas samples are to be stored for more than 24 hours) for each gas and each enclosure to be sampled. One syringe will be used in step 6, one syringe will be used to sample the initial or time-zero concentration, and the remaining five will be used for sampling the gas concentration within the chamber. (See the section "Special Considerations," below, for a more complete description.
5. Instrument for gas analysis. A gas chromatograph (GC) equipped with the appropriate detectors can be used for N_2O, CH_4, and CO_2 analysis; alternatively, an infrared gas absorption (IRGA) analyzer can be used for CO_2 analysis.
6. Four standards for calibration of the GC and a canister of at least one of the standards to transport to the field site for checking the effects of storage and transport on gas concentration.

Procedure

1. Insert the collars into the soil at least 1 week prior to sampling to mitigate placement disturbance. Collars should be inserted 5–10 cm into the soil.
2. Put the enclosure in place and record the time.

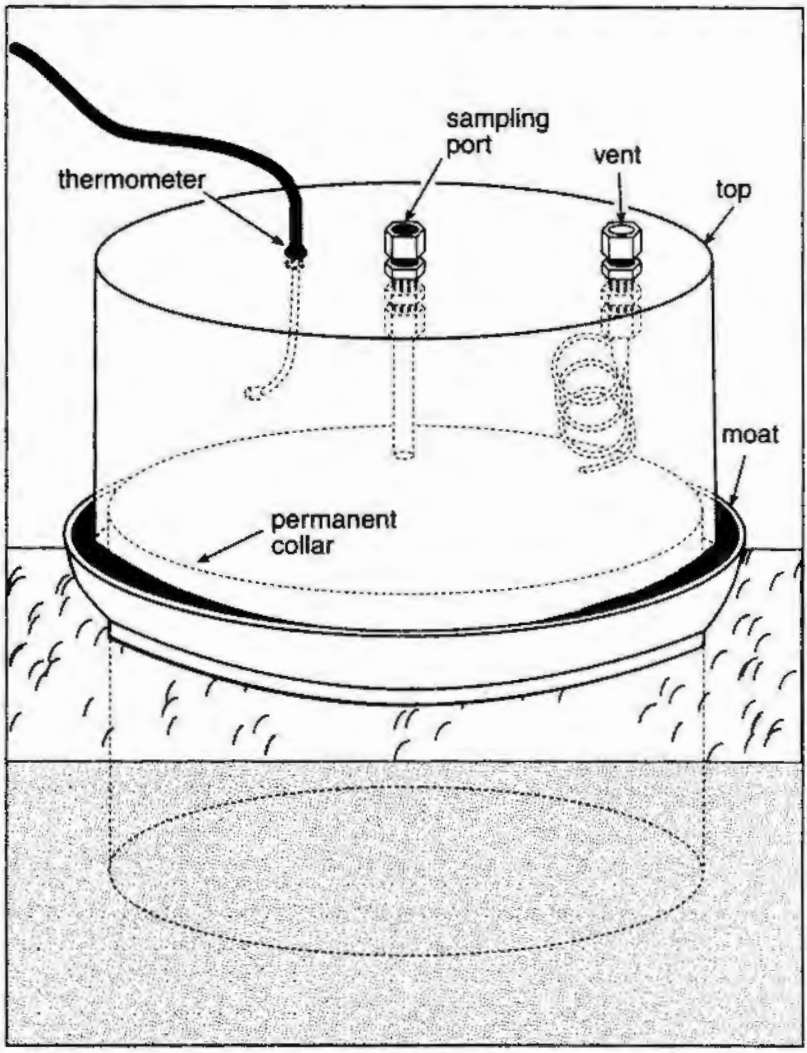

Figure 10.1. The recommended enclosure design including the vent, sampling port, thermometer, and moat for sealing the chamber to its permanent collar. Enclosure, permanent collar, and all fittings should be manufactured with inert materials: PVC, stainless steel, or aluminum. For measurement of reactive trace species, the enclosure can be lined with Teflon, but all materials should be tested to ensure that they do not adsorb, desorb, or otherwise react with the gas of interest. The moat of the permanent collar should be partially (and carefully) filled with water before placement of the enclosure. The water serves as a gas diffusion barrier, thus providing an effective seal. Vent dimensions and sampling port design are detailed in the text. Gastight fittings for the sample port are 1/4 inch Swagelock or Parker fittings. The enclosure can be tested in the laboratory by placing the enclosure in a shallow tray of water and testing for stable gas concentrations over time.

3. Establish the time-zero concentration of the gas by taking 10–20 7–8 mL air samples with a 10 mL syringe equipped with a one-way stopcock.
4. For each gas of interest, sample 7–8 mL of the enclosure volume using a 10 mL syringe equipped with a one-way stopcock valve every 10 minutes for 50 minutes. Record the time of each sampling. This sampling technique has been shown to be sufficient for most situations. In a few cases with very low fluxes, it may be necessary to sample less frequently over a longer period; for cases with very high fluxes, it may be necessary to sample more frequently over a shorter period. The size of the sample taken always exceeds the minimum needed for analysis. For example, a 5 mL sample injection for a 1 mL sample loop is used to ensure that connections and valve are purged with the air sample. We recommend that a single sample be taken for each gas to be analyzed (with the exception of GCs set up for simultaneous injection and analysis).
5. Before removing the enclosure, measure the height of the enclosure over the soil surface in at least four places for each enclosure. Enclosure height must be measured when collars are first used or when disturbed by freeze-thaw or other events.
6. Periodically sample the field standard as for samples.
7. In the laboratory, analyze the sample by gas chromatography. Inject the sample through a valve equipped with a sample loop of the appropriate size (e.g., 1 mL for CH_4 and N_2O and 0.1 mL for CO_2). See section on "Instruments and Other Analytical Considerations," below, for a more detailed discussion.

Analysis and Instruments

Calibration and Standards

Proper instrument calibration and use of standards are common to the analysis of all three gases and require great care. We recommend a four-point calibration with different standards that span the anticipated range of concentrations to be measured including atmospheric concentrations (note that for CH_4 uptake studies, atmospheric concentrations will be the high value). Calibration frequency will depend on the stability of the individual instruments; typically calibration is needed every 15–20 samples. The Environmental Protection Agency (EPA) standard for Quality Assurance/Quality Control (QA/QC) calls for 20% of all analyses to be standards.

All standards must be handled with caution and stored in pressurized containers. Standards should be intercompared against other standards in the laboratory, or other laboratories, and should be traceable to standard gases available from the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards [NBS]). Adequate standards are available from several commercial suppliers (including Matheson Gas Products, P.O. Box 89, 530 Watson Street E., Whitby Ontario, Canada, L1N 5R9; and Scott Specialty Gases, 1290 Combermere St., Troy, MI 48083). Stainless steel regulators should be used to avoid introducing impurities to the standard, and where possible regulators should be dedicated to a specific standard tank (this is essential for reactive compounds like NO and NO_2).

Instrumentation and Other Analytical Considerations

Introduction of a gas sample into the GC may be performed by direct injection through a septum or by use of a two-position gas chromatographic valve with a fixed volume sample loop (Fig. 10.2). We recommend the use of a sample loop connected to a GC sample valve to ensure introduction and analysis of a constant volume of sample. When all gases are to be measured simultaneously, it is useful to purchase and/or reconfigure a GC for simultaneous injection of all the gases. More information on how to do this is available in Sitaula et al. (1992). The detectors can be set up in series or parallel with different considerations for each. However, if the interest is in measuring CO_2 fluxes alone, then consider using a portable CO_2 analyzer.

Carrier gas purity is essential for gas chromatographic analysis of any trace gas but is particularly important for measurement of nitrous oxide and for methane consumption. Purchase of gases that are at least 99.999% pure (ultrahigh purity [UHP]) is recommended. Even so, the two carrier gases commonly used for the measurement of methane:(N_2 and He) are often contaminated by 0.5 ppm of methane against a background of 1.7 ppm (Tab. 10.1). Where necessary, N_2 and He carrier gases can be cleaned of CH_4 either by using an in-line catalytic converter or by passing the carrier gas through a molecular sieve trap (1.27 cm diameter tubing containing coarse mesh molecular sieve, 1.6–3.2 mm [$\frac{1}{16}$ – $\frac{1}{8}$ inch] pellets) placed in a dewar flask containing liquid nitrogen. Traps should be cleaned nightly by placing them, with carrier flow, in a heating mantle filled with silica sand heated to 200 °C.

Carbon dioxide. CO_2 fluxes can be measured by techniques ranging from soda lime absorption of CO_2 to IRGA. Both soda lime and base trap (NaOH and KOH) absorption tend to underestimate high CO_2 fluxes and overestimate low CO_2 fluxes as a result of varying absorption efficiencies (Coleman 1973; Nadelhoffer and Raich 1992; Nay et al. 1994). As a result, we recommend against the use of base traps for routine in situ flux measurements. They can, however, provide an accurate 24-hour integrated flux estimate in some soils, but should be used with caution and at a minimum must be calibrated against instantaneous flux measurements (Nadelhoffer and Raich 1992).

For enclosure measurement of CO_2 fluxes, IRGA analysis is fastest. GC analysis using either a thermal conductivity detector (TCD) or a flame ionization detector (FID and a Carbosieve column) allows simultaneous analysis of more than one gas (Crill et al. 1995). The FID GC technique is similar to that for CH_4 as CO_2 is converted to CH_4 by a methanizer placed before the FID and then measured as CH_4. Methanizers may be purchased commercially (Alltech Associates, Inc. 2051 Waukegan Rd., Deerfield, IL 60015).

Other CO_2 measurement systems include those manufactured by PP Systems, United Kingdom, and Licor Inc., Canada, or Analytical Development Corporation (ADC; http://www.crowcon.com/adc.html). For studies focusing on CO_2 flux alone, a commercial soil respiration chamber linked to an IRGA system (LI-COR, Inc., P.O. Box 4425, Lincoln, NE 68504, http://www.licor.com/index.htm; Norman et al. 1992) may be adequate, although users should be aware that (1) field calibration of the LI-COR (or others) is needed to correct for temperature dependencies of the instrument, (2) the measured flux may be affected by the instrument flow rate

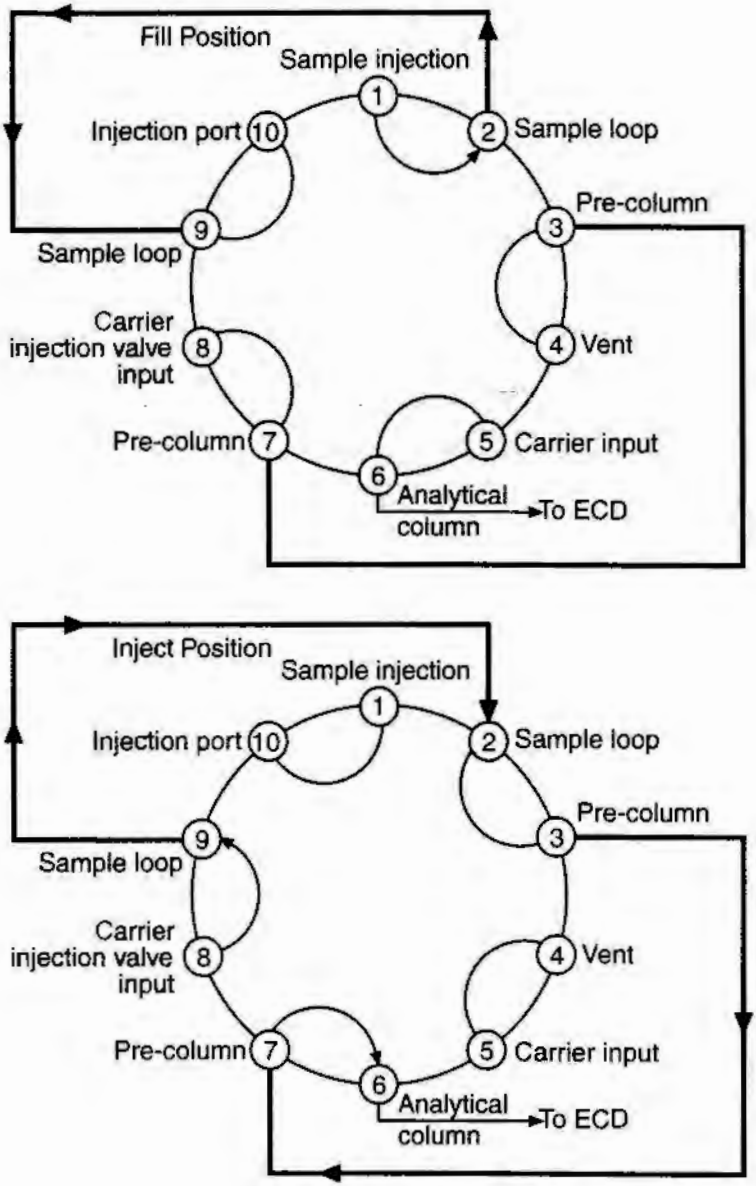

Figure 10.2. Two-position valve layout (with flow diagrams for both positions), including a sample loop, injection and exhaust ports, a pre-column, and an analytical column. Sample is injected into the sample loop with the valve in position 1 (top). Thus, the contents of the sample loop are swept into the pre-column and onto the column when the valve is switched to position 2 (bottom). When the valve is switched back to position 1 (top), the flow in the pre-column is reversed (or back-flushed) and the elements of the gas sample that could prolong the analysis are removed. A simpler six-port valve can be used in cases where a pre-column is not necessary.

because of potential overpressurization of the soil atmosphere, and (3) chamber volumes may be inappropriately small for some soils. Our recommendations assume that the focus of the study is soil or system respiration; to accomplish this, the enclosure must be made of a material that prevents light penetration.

Nitrous oxide. Measurement of N_2O concentrations requires a GC equipped with an electron capture detector (ECD). Gas filter correlation, TDL, IRGA, and photoacoustic IRGA techniques (Ambus and Robertson 1998; Crill et al. 1995) have been applied with varying degrees of success, but the ECD remains the most common and reliable instrument for N_2O analyses. Typically, GC columns used for N_2O analyses are 3–4 m stainless steel tubes (3.175 mm [$\frac{1}{8}$ inch] outer diameter) packed with Porapak QS 60–80 mesh often divided into a 2 m pre-column and a 2 m analytical column. The pre-column allows for faster analyses because air components that are not of interest (water and fluorocarbons) can be flushed off the pre-column, preventing the transfer of later eluting components onto the analytical column. Some ECDs are sensitive to CO_2, allowing simultaneous quantification of CO_2 fluxes. An oxygen/water trap should be placed in the carrier gas line upstream of the GC to prevent damage, because the ECD is susceptible to damage by electrophilic materials including O_2 and freon. Good carrier gases include P5 (95% argon and 5% methane), UHP N_2, and zero air (hydrocarbon-free air). Because copper and brass both react with N_2O, stainless steel fittings, tubing, and valves are required.

Methane. A flame ionization detector in a GC is the most reliable means of measuring methane concentrations, although other techniques, including TDL and gas correlation cells, are available (Crill et al. 1995). One example GC setup includes a 2 m molecular sieve 5A (60–80 mesh), of 2.16 mm inner diameter, with a 0.3 m pre-column to reduce contamination and interference.

Calculations

Calculations of rates of trace gas exchange are based on a difference in the concentration of the gas over time. The calculations required for estimating either net production or net consumption of a trace gas are conceptually straightforward but can be complicated by the fact that the concentration gradient between the soil and the atmosphere begins to diminish immediately upon deployment of the enclosure (Hutchinson and Livingston 1993). Further complications are introduced by the disruption of the atmospheric boundary layer; the importance of these disruptions to the estimated flux increases with the length of time a chamber is in place (Healy et al. 1996). The two factors combined argue for as short a deployment time for the enclosures as logistics will allow. The reader is referred to Livingston and Hutchinson (1995) for a review of trace gas flux calculation considerations.

All measured concentrations should be converted to mass units and corrected to field conditions through application of the Ideal Gas Law:

$$C_m = (C_v \times M \times P)/(R \times T)$$

where

C_m = the mass/volume concentration, e.g., μg CO_2–C/L enclosure, which is equivalent to mg CO_2–C/m^3 enclosure

C_v = the volume/volume concentration (trace gas concentration expressed as a part per million or billion by volume, i.e., ppm_v or ppb_v, respectively, also called mixing ratio), e.g., μL CO_2/L enclosure or ppm_v CO_2

M = the molecular weight of the trace species, e.g., 12 μg CO_2–C/μmol CO_2 or 28 μg N_2O–N/μmol N_2O

P = barometric pressure (P is expressed here in atmospheres), e.g., 1 atm

T = air temperature within the enclosure at the time of sampling, expressed as °K (°K = °C + 273.15)

R = the universal gas constant (0.0820575 L atm·°K·mole)

Thus converted, atmospheric mixing ratios of CH_4 (1.714 ppm_v) and N_2O (311 ppb_v) become 0.855 mg CH_4–C/m^3 and 362 μg N_2O–N/m^3 at standard temperature and pressure (20 °C, 1 atm), and 360 ppm_v CO_2 becomes 179 mg CO_2–C/m^3. The small battery-powered weather stations manufactured by Davis Instruments (Davis Instruments, 3465 Diablo Ave., Hayward, CA 94545; http://www.davis-net.com/) have been particularly helpful for measurements of temperature and barometric pressure, but see also Chapter 3, this volume. If barometric pressure and temperature do not change significantly over the course of the enclosure measurement period (the usual case), it is not necessary to measure either variate precisely to accurately calculate a gas flux.

The converted concentration values are then used to calculate the flux of interest. The most commonly used equation assumes a constant flux (f) and a linear increase in trace gas conceutration (C) over time (t):

$$f = V \times C_{rate}/A$$

where

f = gas flux as mass·m^{-2}·h^{-1}, e.g., mg CO_2–C·m^{-2}·h^{-1}

V = the internal volume of the enclosure, including collar volume, expressed as m^3

A = the soil area the enclosure covers, expressed as m^2

C_{rate} = change in concentration of gas (C_m) over the enclosure period, expressed as mass·m^{-3}·h^{-1}, e.g., mg CO_2–C·m^{-3}·h^{-1}

The calculation of gas concentration change should include only data for the time period of linearly increasing trace gas concentrations in the chamber. Thus, C_{rate} is the slope of the best-fit line for the regression of gas concentration (mass/m^3) versus time (h). Each flux series should be graphed and evaluated for linearity; individual point measurements should be carefully checked and discarded if outside confidence bounds. The change in gas concentration within an enclosure will taper off after some period of time, and inclusion of points taken after this period can lead to underestimates of the flux. The recommended units for expression of the flux are μg N_2O–N·m^{-2}·h^{-1}, mg CH_4–C·m^{-2}·h^{-1}, and mg CO_2–C·m^{-2}·h^{-1}.

Special Considerations

Enclosure and Collar Construction and Design

The objectives of enclosure design are to be as noninvasive as possible, and to avoid pressure or temperature changes and excessive trace gas concentration increases. Enclosures are constructed in two parts: (1) a permanent collar, which is put in place prior to sampling and left in place for the duration of the sampling period (in some cases years), and (2) the enclosure itself, which is placed on the collar (over the soil) for the short period over which gas samples are removed (usually an hour or so; Fig. 10.1).

A thorough discussion of chamber geometry is provided in Matthias et al. (1978). The enclosure's surface area to volume ratio determines its sensitivity. A rectangular or cylindrical rigid enclosure (usually 500–900 cm^2) is typical. The surface area should be designed to minimize soil disturbance. Larger surface areas have the advantage of capturing more of the local soil heterogeneity. All construction materials (including sealants) must be made of inert materials that do not react or "bleed" with the gases to be measured. Aluminum, stainless steel, and PVC (which must be opaque to prevent light penetration and temperature rises) have been used successfully for measurement of the nonreactive gases considered here (but may not be suitable for measurement of NO_x, NH_x, and some VOCs and sulfur species). Sealants should always be tested for gas production or interference before use—e.g., different formulations of silicone caulk can differentially bleed N_2O, consume CH_4, or produce interfering peaks upon GC-ECD analysis.

Aluminum and stainless steel collars can be machined, and plastic can be molded to include a channel or "moat" that can be filled with water to provide a gastight seal between the enclosure and the permanent collar. In some cases, a water-filled moat may not be appropriate (e.g., where the landscape is steeply sloped or when the experimental objectives require winter sampling). In these cases, we recommend that the enclosure fit tightly over the ring and be sealed on the outside by elastic material (e.g., a rubber bicycle tube).

Enclosure sampling ports are typically a swagelock fitting with a septum (e.g., Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015; stock no. 15418) attached to a piece of stainless steel tubing that extends sufficiently far into the enclosure to allow sampling of the well-mixed atmosphere in the enclosure's center. A vent tube volume of between 15 and 35 cm^3 is adequate for most barometric conditions and enclosures (Hutchinson and Mosier 1981).

The preferred design of an enclosure includes a sampling port, a properly sized vent, a permanent collar, and a moat to provide a gastight seal between the permanent collar and enclosure (Fig. 10.1). When using the recommended permanent collar and enclosure design it is useful to establish how the gas fluxes change over time following the placement of the collar, particularly for shorter-term studies of a few weeks to months. In cases where the experimental goal is short-term measurement of fluxes from a remote site, it may be desirable to use more portable enclosures that have a skirt secured by an inner tube filled with sand. Again, however, these sorts

of measurements are likely to be complicated by difficulties in establishing a gas-tight seal between the soil and atmosphere.

Enclosure Considerations

Leaks, mixing, and temperature control problems are common to all enclosures. The leaks are likely to occur in two locations: where the enclosure top meets the base (prevented by use of the moat sealing system depicted in Figure 10.1) or where base ring meets the soil. Leakage may be a greater problem in very dry soil because air-filled pore space increases dramatically, but leakage under most circumstances will be minimal from a vented static enclosure so long as temperature differences (between the inside and outside of the enclosure) are small (approx. 1 °C) and sampling periods are short (<1 hour). Temperature differences between the ambient air outside the enclosure and the air within the chamber can be minimized by reducing deployment time, by constructing the enclosure out of a light-colored material (e.g., white PVC), or by covering the enclosure with reflective insulation.

Disturbance of the enclosure site can be a problem for all trace gases. Insertion of a permanent collar that allows repeated sampling of the same location may cause substantial root damage in some sites, so collars should be put in place at least 1 week prior to sample collection. Soil disturbance (e.g., compaction) associated with collar placement or sampling activities should be minimized; frequent sampling may require a semipermanent boardwalk or other protective platform. Internal pressures generated by heavy footsteps near enclosures over organic soils (such as those where methane is commonly measured) can force gases out of the soil.

Sampling Considerations

Polypropylene syringes (available from medical suppliers) are inexpensive, allow the generation of the pressure differential required for extraction of a sample, and usually present minimal contamination problems when pretreated (Mosier and Klemedtsson 1994). Nylon syringes have been tested and used successfully but are more expensive. Algal growth in glass syringes has been reported in wet or humid environments.

All butyl rubber products, including the plungers of syringes, can adsorb and desorb gases and therefore need to be conditioned to avoid contamination of CH_4 and N_2O samples in particular; this is easily done by baking separated plungers and barrels at 50–55 °C overnight.

Sample storage in syringes should be limited (not more than 24 hours) because gases diffuse through the polypropylene walls of the syringe (see section on "Sample Storage," below). Nylon one-way stopcock valves (Baxter catalog no. K71, Baxter Diagnostics Inc., Scientific Products Division, 1430 Waukegan Road, McGaw Park, IL 60085-6787) are recommended for sealing syringes during transport; alternatively, silicone stoppers can be placed over the needle. Side-port needles to avoid needle coring are preferred but are not mandatory. Pressure differences during transport can cause leakage where field temperatures are different from laboratory temperatures, where samples are flown from the field to the laboratory, or when samples are transported across different elevations. To protect against such

changes, the syringe can be slightly pressurized with a rubber band over the syringe and plunger. Where samples are stored in vials rather than syringes, vials can be overpressurized with excess gas during sampling. As a further precaution, the field standard canister should be sampled in the field and treated as a sample.

Sampling Strategy

Successful enclosure sampling requires consideration of several temporal scales. First is the number of samples and frequency of sampling once the enclosure is put in place. We recommend a deployment time of no shorter than 4–5 minutes and no longer than 1 hour. Continuous sampling instruments (e.g., CO_2 using a flow-through IRGA system connected to a data logger) have shown that fluxes are usually perturbed for the first 30–60 seconds following the placement of the enclosure, probably due to the pressure fluctnations induced by the enclosure placement. The period over which sampling should occur is the period over which there is a linear increase in gas concentration over time. Usually an hour is sufficient to document a significant flux. The potential influence of deployment time on the calculated flux has been evaluated by Healy et al. (1996), who have shown that long deployment times lead to significant underestimates of the flux.

Sample Storage

When samples need to be stored prior to analysis, it is critical to store sample standards in the same way as field samples to identify potential problems. Storage should be approached carefully. Sealed glass or polished stainless steel containers are best for long-term storage but are prohibitively expensive for the large sample numbers required for enclosure flux measurements (Tans et al. 1989). Less expensive alternatives include Venoject and Vacutainer blood sampling vials, but these suffer from differential (cross-batch) problems with sample absorption, leakage, and contamination of the samples during vial processing, and contamination caused by the butyl rubber seals. Boiling the butyl rubber seals in water for 20–30 minutes usually minimizes contamination problems, but not always; we recommend against the use of blood sampling vials altogether. As a word of caution, the manufacture of Vacutainers in particular can include processing in an atmosphere of N_2O. A more extensive discussiou of the problems associated with sample storage is provided in Mosier and Klemedtsson (1994). Crimp-top vials designed for automated analysis of headspace volumes and Wheaton serum vials have been used successfully in some laboratories, but each batch of septa material must be carefully evaluated for absorption and contamination. All storage containers should be adequately purged with inert gas and evacuated before use or purged with sample to minimize cross-contamination.

Miscellaneous Considerations

Enclosure-to-enclosure variation in fluxes is considerable, and the resulting measurements are usually not normally distributed. Estimates of the number of enclo-

sures reqnired to characterize the flux of a trace gas from a given area range between 50 and 100 depending on the flux: the larger the flux, the greater the variance (Starr et al. 1995; Robertson 1993; Parkin 1987; Bnrton and Beauchamp 1985; Foloronuso and Rolston 1984; Robertson and Tiedje 1984). Because of labor and time constraints, only rarely are a sufficient number of enclosures deployed for confident characterization of a site. Flux measurements often follow a Poisson density function with a few high values and increasing variance with increasing flux (Matson et al. 1990). As a result, the measurements should be analyzed with the appropriate statistical techniques that accommodate nonnormally distributed data (see Chapter 1, this volume).

Fluxes of all of these gases can vary diurnally, seasonally, and interannually depending on climate, substrate availability, and the rates of the processes responsible for producing and consuming the gases. Diurnal changes in fluxes can be substantial and should be evaluated for individual sites (Mosier et al. 1991). The overall sampling strategy should build on the soil information available at a given site and be sufficiently specific to address the scientific question posed (see Chapter 1, this volume). In many cases, gas fluxes peak during seasonal transitions or immediately following precipitation or fertilization. If the goal of the study is to develop an annual estimate of flux, the *minimum* sampling requirement is once per month with more frequent sampling during the time of peak flux. For sites where the peak flux is in the spring, this requires increasing the sampling frequency to weekly or biweekly. For sites where peak fluxes follow precipitation or fertilization, hourly sampling may be required to fully characterize the response. In all cases, decisions about sampling frequency should be based on the understanding of the dynamics of the underlying processes and the objective of the study (see Chapter 14, this volume, for discussion of denitrification; Chapter 11, this volume, for discussion of decomposition; and Chapter 13, this volume, for discussion of C and N mineralization and nitrification).

Ancillary Data

Other ancillary measurements helpful to the interpretation of trace gas measurements include soil temperature at the surface and at 2.5 and 5 cm, and water-filled pore space (see Chapter 3, this volume); soil organic carbon and nitrogen content of the surface layers (see Chapter 5, this volume); soil texture (see Chapter 4, this volume); and N mineralization and mineralizable carbon (see Chapter 13, this volume). Soil pH and redox are particularly helpful for interpretation of methane production.

Acknowledgments James Sulzman assisted with the preparation of the final manuscript. Pamela Matson, Elizabeth Sulzman, Peter Harley, and three anonymous reviewers provided thorough and thoughtful reviews that significantly enhanced the quality of this manuscript. E. A. Holland acknowledges the suppon of NCAR and the Niwot Ridge NSF LTER program during the completion of this manuscript. The National Center for Atmospheric Research is sponsored hy the National Science Foundation.

References

Ambus, P., H. Clayton, J. M. R. Arah, K. A. Smith, and S. Christensen. 1993. Similar N_2O flux from soil measured with different chamber techniques. *Atmospheric Environment* 27:121–123.

Ambus, P., and G. P. Robertson. 1998. Automated near-continuous measurement of CO_2 and N_2O fluxes with a photoacoustic infrared spectrometer and flow-through soil cover boxes. *Soil Science Society of America Journal* 62:394–400.

Aselmann, I., and P. J. Crutzen. 1989. Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions. *Journal of Atmospheric Chemistry* 8:307–359.

Baldocchi, D. D. 1991. Canopy control of trace gas emissions. Pages 293–333 *in* T. D. Sharkey, E. A. Holland, and H. A. Mooney, editors, *Trace Gas Emissions by Plants.* Academic Press, San Diego, California, USA.

Burton, D. L., and E. G. Beauchamp. 1985. Denitrification rate relationships with soil parameters in the field. *Communications Soil Science Plant Analysis* 16:539–549.

Businger, J. A., and S. P. Oncley. 1990. Flux measurement with conditional sampling. *Journal of Atmospheric and Oceanic Technology* 7:349–352.

Christensen, S., P. Ambus, and F. G. Wienhold. 1996. Nitrous oxide emission from an agricultural field: comparison between measurements by flux chamber and micrometeorological techniques. *Atmospheric Environment* 30:4183–4189.

Coleman, D. C. 1973. Compartmental analysis of total soil respiration; an exploratory study. *Oikos* 24:195–199.

Crill, P., J. H. Butler, D. J. Cooper, and P. C. Novelli. 1995. Standard analytical methods for measuring trace gases in the environment. Pages 164–205 *in* P. A. Matson, editor, *Biogenic Trace Gases: Measuring Emissions from Soil and Water.* Blackwell Science, Cambridge, UK.

Denmead, O. T. 1979. Chamber systems for measuring nitrous oxide emission from soils in the field. *Soil Science Society of America Journal* 43:89–95.

Desjardins, R., R. Hart, J. Macpherson, P. Schuepp, and S. B. Verma. 1992. Aircraft- and tower-based fluxes of carbon dioxide, latent and sensible heat. *Journal of Geophysical Research* 97:18,477–18,485.

Desjardins, R., P. Rochette, and E. Puttey. 1993. Measurement of greenhouse gas fluxes using aircraft and tower based techniques. *In* L. A. Harper, A. R. Mosier, J. M. Duxbury, and D. E. Rolston, editors, *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change.* American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, Wisconsin, USA.

Foloronuso, O. A., and D. E. Rolston. 1984. Spatial variability of field-measured denitrification gas fluxes. *Soil Science Society of America Journal* 48:1214–1219.

Goulden, M. L., J. W. Munger, and S. C. Wofsy. 1996. Exchange of carbon dioxide by a deciduous forest: response to interannual climate variability. *Science* 271:1576–1579.

Hargreaves, K. J., F. G. Wienhold, L. Klemedtsson, J. R. M. Arah, I. J. Beverland, D. Fowler, B. Galle, D. W. T. Griffith, U. Skiba, K. A. Smith, M. Welling, and G. W. Harris. 1996. Measurement of Nitrous Oxide emission from agricultural land using micrometeorological methods. *Atmospheric Environment* 30:1563–1571.

Healy, R. W., R. G. Striegl, T. F. Russell, G. L. Hutchinson, and G. P. Livingston. 1996. Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange: identification of physical processes. *Soil Science Society of America Journal* 60:740–749.

Holland, E. A., B. H. Braswell, J.-F. Lamarque, A. Townsend, J. M. Sulzman, J.-F. Müller, F.

Dentener, G. Brasseur, H. I. Levy, J. E. Penner, and G. Roelofs. 1997. Variations in the predicted spatial distribution of atmospheric nitrogen deposition and their impact on carbon uptake by terrestrial ecosystems. *Journal of Geophysical Research* 102:15,849–15,866.

Hutchinson, G. L., and G. P. Livingston. 1993. Use of chamber systems to measure trace gas fluxes. *In* L. A. Harper, A. R. Mosier, J. M. Duxbury, and D. E. Rolston, editors, *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change.* American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, Wisconsin, USA.

Hutchinson, G. L., and A. R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45:311–316.

IPCC. 1995. *Climate Change 1994 Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios.* Cambridge University Press, Cambridge, UK.

Jury, W. A., J. Letey, and T. Collins. 1982. Analysis of chamber methods used for measuring nitrous oxide production in the field. *Soil Science Society of America Journal* 46:250–256.

Kanemasu, E. T., W. L. Powers, and J. W. Sij. 1974. Field chamber measurements of CO_2 flux from soil surface. *Soil Science* 118:233–237.

Kolb, C. E., J. C. Wormhoudt, and M. S. Zahniser. 1995. Recent advances in spectroscopic instrumentation for measuring stable gases in the natural environment. Pages 259–290 *in* P. A. Matson and R. C. Harriss, editors, *Biogenic Trace Gases: Measuring Emissions from Soil and Water.* Blackwell Science, Cambridge, Massachusetts, USA.

Lenschow, D. H. 1995. Micrometeorlogical techniques for measuring biosphere-atmosphere trace gas exchange. Pages 126–163 *in* P. A. Matson and R. C. Harriss, editors, *Biogenic Trace Gases: Measuring Emissions from Soil and Water.* Blackwell Science, Cambridge, Massachusetts, USA.

Livingston, G. P., and G. L. Hutchinson. 1995. Enclosure-based measurements of trace gas exchange: applications and sources of error. Pages 14–51 *in* P. A. Matson and R. C. Harriss, editors, *Biogenic Trace Gases: Measuring Emissions from Soil and Water.* Blackwell Science. Cambridge, Massachusetts, USA.

Matson, P. A., and R. C. Harriss, editors. 1995. *Biogenic Trace Gases: Measuring Emissions from Soil and Water. Methods in Ecology.* Blackwell Science, Cambridge, Massachusetts, USA.

Matson, P. A., P. M. Vitousek, G. P. Livingston, and N. A. Swanberg. 1990. Sources of variation in nitrous oxide flux from Amazonian ecosystems. *Journal of Geophysical Research* 95:16789–16798.

Matthias, A. D., D. N. Yarger, and R. S. Weinbeck. 1978. A numerical evaluation of chamber methods for determining gas fluxes. *Geophysical Research Letters* 5:765–768.

Mosier, A. R., D. Schimel, D. Valentine, K. Bronson, and W. Parton. 1991. Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands. *Nature* 350:330–332.

Mosier, A. R., and L. Klemedtsson. 1994. Measuring denitrification in the field. Pages 1047–1066 *in* R. W. Weaver et al., editors, *Methods of Soil Analysis. Part 2, Microbiological and Biochemical Properties.* Soil Science Society of America, Madison, Wisconsin, USA.

Nadelhoffer, K. J., and J. W. Raich. 1992. Fine root production estimates and belowground carbon allocation in forest ecosystems. *Ecology* 73:1139–1141.

Nay, S. M., K. G. Mattson, and B. T. Bormann. 1994. Biases of chamber methods for measuring soil CO_2 efflux demonstrated with a laboratory apparatus. *Ecology* 75:2460–2463.

Norman, J. M., R. Garcia, and S. B. Verma. 1992. Soil Surface CO_2 fluxes and the carbon budget of a grassland. *Journal of Geophysical Research* 97D:18,845–18,853.

Parkin, T. B. 1987. Soil microsites as a source of denitrification variability. *Soil Science Society of America Journal* 51:1194–1199.

Robertson, G. P. 1993. Fluxes of nitrous oxide and other nitrogen trace gases from intensively managed landscapes: a global perspective. *In* L. A. Harper, A. R. Mosier, J. M. Duxbury, and D. E. Rolston, editors, *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, Madison, Wisconsin, USA.

Robertson, G. P., and J. M. Tiedje. 1984. Denitrification and nitrous oxide production in old growth and successful Michigan forests. *Soil Science Society of America Journal* 48:383–389.

Schimel, D. S., B. H. Braswell, and W. J. Parton. 1997. Equilibration of the terrestrial water, nitrogen and carbon cycles. *Proceedings of the National Academy of Sciences* [USA], 94:8280–8283.

Sitaula, B. K., L. Jiafa, and L. R. Bakken. 1992. Rapid analysis of climate gases by wide bore capillary gas chromatography. *Journal of Environmental Quality* 21:493–496.

Starr, J. L., T. B. Parkin, and J. J. Meisinger. 1995. Influence of sample size on chemical and physical soil measurements. *Soil Science Society of America Journal* 59:713–719.

Tans, P. P., T. J. Conway, and T. Nakazawa. 1989. Latitudinal distribution of the sources and sinks of atmospheric carbon dioxide derived from surface observations and an atmospheric transport model. *Journal of Geophysical Research* 94D:5151–5172.

Wofsy, S. C., M. L. Goulden, and J. W. Munger. 1993. Net exchange of CO_2 in a mid-latitude forest. *Science* 260:1314–1317.